

CARBON / CARBONATE GEOCHEMISTRY

Introduction

Basic organic geochemical analyses were performed to support the general scientific objectives of the ODP (Ocean Drilling Program). Elemental carbon data obtained from samples contributed to a wide range of studies. Carbonate contents of cores were used for sedimentological and lithostratigraphic classification purposes. Organic carbon content (coming from organic matter) provided valuable evidence for ocean paleoenvironmental studies and depositional environment classification. Carbon to nitrogen ratios were used to infer the nature of the organic matter (e.g., land or aquatic plant material) preserved in cores. Molecular organic geochemical analyses such as alkenone unsaturation can be used to infer marine paleotemperature information.

One of the reasons for performing carbon analyses was to monitor for hydrocarbons. Although much of the carbon in sediments was in the form of inorganic carbon or carbonate, most of the interest was in the organic carbon – that carbon coming from marine phytoplankton, bacteria, algae and other organic material. The *JOIDES Resolution (JR)* was not designed to drill into pressurized reservoirs of oil or gas, so constant monitoring for hydrocarbons was required. Maturation of organic material in undersea environments may result in hydrocarbon generation, so sediments were monitored for increasing amounts of organic carbon.

Data Acquisition

Many diagenetic changes occur in the top 150 m of the sediment column which was one of the reasons for higher density sampling of the first 10 – 15 cores in a hole. During the first part of the ODP, 25-30 cm whole core samples (Organic Geochemistry – OG) were taken every 30 m and immediately frozen to preserve the core because of the volatile nature of organic matter. Not all analyses could be done in the shipboard chemistry lab, and freezing these samples would slow down deterioration of the organic matter and minimize chances of contamination. Shipboard scientists stop taking OG samples after Leg 134 probably because they were able to collect the information they needed, and there were few requests for OG samples for shore-based studies.

Analyses of samples produced data as weight percentages of total carbon, inorganic carbon, and organic carbon (directly or by difference). Although other carbonates may be present, all acid-soluble (inorganic) carbon was reported as calcium carbonate. In addition, analyses sometimes included data for elemental concentrations of sulfur, nitrogen and hydrogen. These data were used to characterize the nature of the organic carbon.

Samples taken for carbon analysis were freeze-dried, crushed and carefully weighed. If the sample was to be analyzed for carbonate, the sample was mixed with acid to

convert the carbonate to CO₂ before analysis in the coulometer. Samples to be analyzed using a CHNS analyzer for total carbon, nitrogen and sulfur were mixed with an oxidizer and combusted at 1000 °C. The table below briefly outlines the variety of instruments used to collect organic and inorganic carbon data during the ODP.

Table 1: Instruments used for Carbon Analyses

Instrument	Analytical Result
Carbonate Bomb	carbonate carbon – CaCO ₃
Perkin Elmer 240C CHN Elemental Analyzer	total carbon, nitrogen, sulfur
Coulometrics 5020 Total Carbon Apparatus	total carbon
Coulometrics 5030 Carbonate Carbon Apparatus	inorganic carbon (carbonate)
Coulometrics 5011 Coulometer	organic and inorganic carbon
Carlo Erba CNS Elemental Analyzer 1106	total carbon, nitrogen, sulfur, hydrogen
Carlo Erba NA 1500 CNS Analyzer	total carbon, nitrogen, sulfur, hydrogen

Additional information about carbon measurements can be found in Technical Note 30: Introduction to Shipboard Organic Geochemistry on the *JOIDES Resolution*.

Archive

Pre-Janus Archive

Early in the ODP, carbonate data were collected on logsheets which were sent back to ODP/TAMU at the end of each cruise. The data were entered into an S1032 database and the logsheets were microfilmed for archival storage. Data entry routines were implemented so that data entry could be done on the ship. Carbonate data were stored in the S1032 database until the Janus database became operation on Leg 171.

Migration of carbonate data to Janus

The data model for carbonate data can be found in Appendix I. Included are the relational diagram and the list of the tables that contain data pertinent to Carbonates, the column names and the definition of each column attribute. ODP Information Services Database Group was responsible for the migration of pre-Leg 171 data to Janus.

Janus Carbonate Data Format

Carbonate analyses can be retrieved from Janus Web using a predefined query. The Carbonate query webpage allows the user to extract data using the following variables to restrict the amount of data retrieved: leg, site, hole, core, section, depth ranges, or latitude and longitude ranges.

Table 2 lists the data fields retrieved from the Janus database for the Carbonates predefined query. The first column contains the data item; the second column indicates the Janus table or tables in which the data were stored; the third column is the Janus column name or the calculation used to produce the value. Appendix II contains additional information about the fields retrieved using the Janus Web Carbonates query, and the data format for the archived ASCII files.

Table 2. Carbonates query

Item Name	Janus Table	Janus Column Name and Calculation
Leg	SECTION	Leg
Site	SECTION	Site
Hole	SECTION	Hole
Core	SECTION	Core
Coretype	SECTION	Core_type
Section	SECTION	Section_number
Top Interval	SAMPLE	Top_Interval x 100
Bottom Interval	SAMPLE	Bottom_Interval x 100
Depth (mbsf)	DEPTH_MAP, SAMPLE	DEPTH_MAP.Map_interval_top + SAMPLE.Top_interval
Inorganic Carbon Percent	CHEM_CARB_ANALYSIS	Analysis_code - INOR_C::Analysis_result
CaCO ₃ Percent	CHEM_CARB_ANALYSIS	Analysis_code - CaCO3::Analysis_result
Total Carbon Percent	CHEM_CARB_ANALYSIS	Analysis_code - TOT_C::Analysis_result
Organic Carbon Percent	CHEM_CARB_ANALYSIS	Analysis_code - ORG_C::Analysis_result
Nitrogen Percent	CHEM_CARB_ANALYSIS	Analysis_code - NIT::Analysis_result
Sulfur Percent	CHEM_CARB_ANALYSIS	Analysis_code - SUL::Analysis_result
Hydrogen	CHEM_CARB_ANALYSIS	Analysis_code - H::Analysis_result

Data Quality

The Carbonate data in Janus represents an extensive collection of inorganic and organic carbon in sediments from ocean basins throughout the earth. Over 66,000 samples were analyzed for inorganic and organic carbon. There are few known instances where there was any major problem with data collection. Anything written or typed was a potential source of errors. Analytical results were written on logsheets. These data were then typed into S1032. Data entry programs were implemented to add the data to S1032, but it still required manual entry. Data acquisition programs were later implemented to collect carbon data, but the operator manually entered the sample information. Writing down or typing incorrect information occasionally happened, and some mistakes were not identified. Often, the scientific party found errors and corrected them for the data included in the Initial Report volume, but data sent back to ODP/TAMU did not get corrected.

Another error found during the migration of carbon data was that samples were missing from the database. In those instances, a sample was entered into the database so that the data could be migrated. The verification of those samples and the verification of the entire carbonate data set were not completed due to time constraints. Most data

collected after the Janus database was operational on Leg 171 were verified as part of the Janus data management and verification procedures (see Metadata Introduction). Some verification was done on the pre-Leg 171 data; however, if there is a discrepancy between the database and data in the Initial Report volumes, the published data should be considered more reliable.

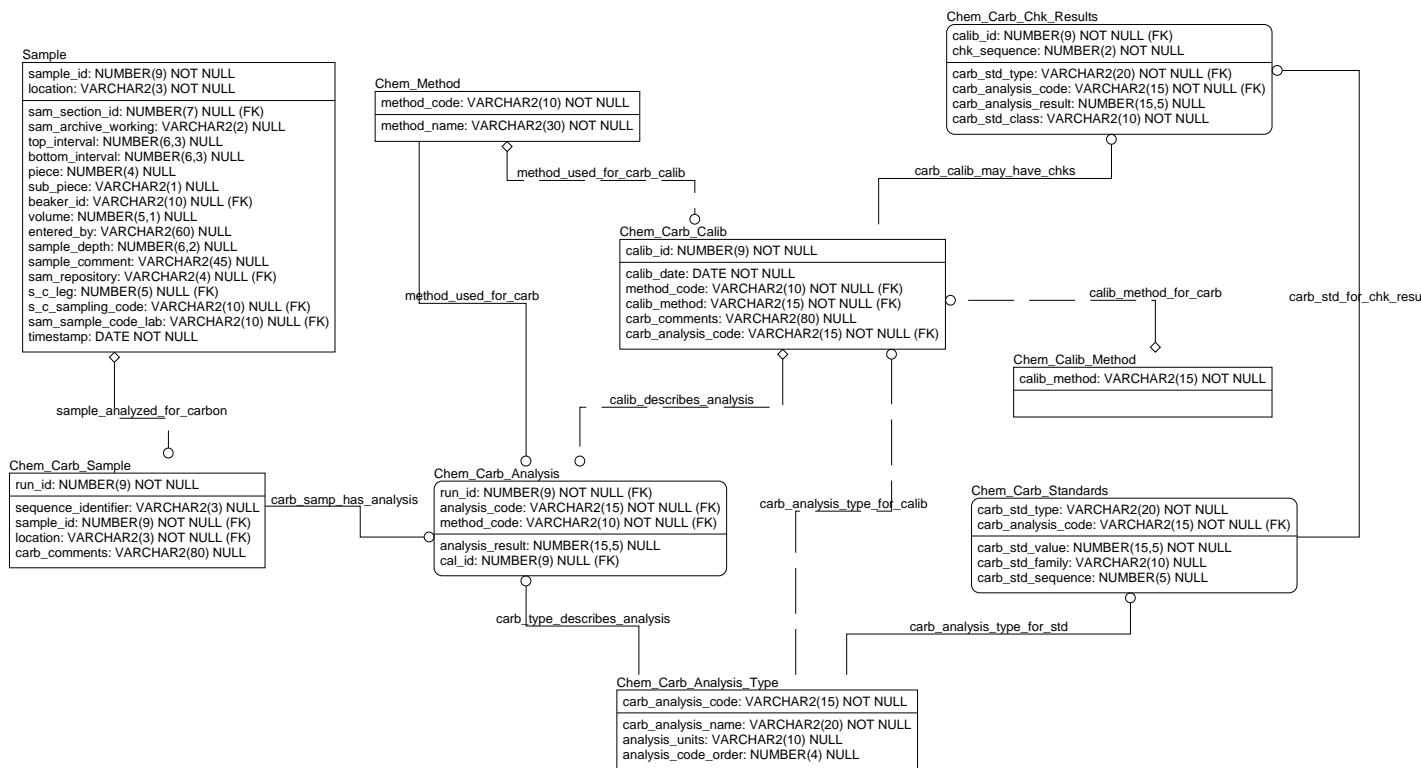
Janus does not contain any calibration information for carbonates. Procedures for storing calibration information were not implemented during the ODP.

References

Emeis, K., and Kvenvolden, K.A., 1986. Shipboard Organic Geochemistry on *JOIDES Resolution*, ODP Tech. Note No. 7.

Kvenvolden, K.A., and McDonald, T.J., 1986. Organic Geochemistry on the *JOIDES Resolution*--An Assay, ODP Tech. Note No. 6.

Pimmel, A., and Claypool, G., 2001, Introduction to Shipboard Organic Geochemistry on the *JOIDES Resolution*. ODP Tech. Note 30.



APPENDIX I: Janus Data Model – Carbonate Chemistry - CARB

Carbonate Chemistry - CARB		
Table Name	Column Name	Column Comment
Chem_Carb_Sample	run_id	Unique Oracle-generated sequence identifier that will allow duplicate analyses of a sample to be entered into database.
	sequence_identifier	Number indicating order in which analyses were run when duplicate analyses are stored.
	sample_id	Oracle-generated sequence number that with <i>location</i> uniquely identifies a sample.
	location	Code that indicates which Janus application assigned the sample_id. Used with <i>sample_id</i> to uniquely identify a sample.
	carb_comments	Comment concerning a carbonate analysis.
Chem_Carb_Analysis	run_id	Unique Oracle-generated sequence identifier that will allow duplicate analyses from a sample to be entered into database.
	analysis_code	Code describing the type of analysis for which a sample was analyzed.
	method_code	A code for the method or instrument used to analyze a sample.
	analysis_result	Numerical result of the analysis of a sample.
	cal_id	Oracle-generated sequence number for a carbonate calibration run.
Chem_Carb_Analysis_Type	carb_analysis_code	Code describing the type of analysis for which a sample can be analyzed.
	carb_analysis_name	Full name or description of analysis type.
	analysis_units	The reported measurement units of the analysis result.
	analysis_code_order	Number defining the order that analysis codes and results will appear on a spreadsheet or report.
Chem_Method	method_code	A code for the method or instrument used for analyzing a sample.
	method_name	The name of the method or instrument used for analyzing a sample.
Chem_Carb_Calib	calib_id	Oracle-generated sequence number for a carbonate calibration run.
	calib_date	The date and time of a calibration run.
	method_code	A code for the method or instrument used for analyzing a sample.
	calib_method	Method used for calibrating the analytical instrument.
	carb_comments	A comment concerning a carbonate calibration.
	carb_analysis_code	Code describing the type of analysis for which a sample can be analyzed.
Chem_Calib_Method	calib_method	Method used for calibrating the analytical instrument.
Chem_Carb_Chk_Results	calib_id	Oracle-generated sequence number for a carbonate calibration run.
	chk_sequence	Number indicating order of measurements.
	carb_std_type	The name of the carbonate standard used.
	carb_analysis_code	Code describing the type of analysis for which a sample can be analyzed.
	carb_analysis_result	The result of the analysis of a sample or standard.
	carb_std_class	Code describing type of check analysis as a standard, blank, or unknown check
Chem_Carb_Standards	carb_std_type	The name of the carbonate standard used.
	carb_analysis_code	Code describing the type of analysis for which a sample can be analyzed.
	carb_std_value	The value of a carbonate standard for a particular analysis code.
	carb_std_family	Name for group of carbonate standards.
	carb_std_sequence	
Section	section_id	Unique Oracle-generated sequence number to identify each section. This is done because of the physical subsection / zero section problems. In adding new sections, deleting sections or changing sections - don't want to have to renumber.

Carbonate Chemistry - CARB		
Table Name	Column Name	Column Comment
	leg	Number identifying the cruise for which data were entered into the database.
	site	Number identifying the site from which the core was retrieved. A site is the position of a beacon around which holes are drilled.
	hole	Letter identifying the hole at a site from which a core was retrieved or data were collected.
	core	Sequential numbers identifying the cores retrieved from a particular hole. Cores are generally 9.5 meters in length, and are numbered serially from the top of the hole downward.
	core_type	A letter code identifying the drill bit/coring method used to retrieve the core.
	section_number	Cores are cut into 1.5 m sections. Sections are numbered serially, with Section 1 at the top of the core.
	section_type	Used to differentiate sections of core (S) from core catchers (C). Previously core catchers were stored as section CC, but in Janus core catchers are given the next sequential number from the last section recovered.
	curated_length	The length of the section core material, in meters. This may be different than the liner length for the same section. Hard rock cores will often have spacers added to prevent rock pieces from damaging each other.
	liner_length	The original length of core material in the section, in meters. Sum of liner lengths of all the sections of a core equals core recovery.
	core_catcher_stored_in	Sometimes the core catcher is stored in a D tube with a section. core_catcher_stored_in contains the section number of the D tube that holds the core catcher.
	section_comments	Comments about this section
Sample		
	sample_id	Oracle-generated sequence number that with <i>location</i> uniquely identifies a sample.
	location	Code that indicates which Janus application assigned the sample_id. Values are SHI (ship), GCR (Gulf Coast Repository), ECR (East Coast Repository), WCR (West Coast Repository) and BCR (Bremen Core Repository). Used with <i>sample_id</i> to uniquely identify a sample.
	s_c_leg	Number identifying the cruise for which data were entered into the database. Foreign key used with <i>s_c_sampling_code</i> to link samples with a scientist's sample request.
	s_c_sampling_code	Code used to identify samples taken for a sample request. Used with <i>s_c_leg</i> .
	sam_archive_working	Part of section where sample was taken. Valid values: WR – whole round, A – archive half, W – working half.
	top_interval	Distance in meters from the top of the section to the top of the sample.
	bottom_interval	Distance in meters from the top of the section to the bottom of the sample.
	piece	Additional identifier for hard rock samples. Each individual piece of rock within a section is numbered consecutively starting at the top of the section.
	sub_piece	Additional identifier for hard rock samples. When a piece is broken, the individual fragments are given consecutive letter designations. Note that subpiece assignments must be made in conjunction with piece numbers.
	beaker_id	The number on the moisture density beaker. Used for samples analyzed for moisture and density.
	volume	Volume of sample.
	entered_by	Indicates who entered the sample into the database.
	sample_depth	Depth of the sample.
	sample_comment	Comment about the sample.
	sam_repository	Repository where sample was taken. Valid values SHIP (ship), GCR (Gulf Coast Repository), ECR (East Coast Repository), WCR (West Coast Repository) and BCR (Bremen Core Repository).
	sam_sample_code_lab	Code to indicate the shipboard lab that will perform the initial analysis.
	sam_section_id	unique Oracle-generated sequence number to identify each section. This is a foreign key that links a sample to leg, site, hole, core, and section.
	timestamp	Date and time when sample was entered into database. Samples taken before November 25, 1998 and migrated samples have the timestamp 11/25/1998 12:26 PM.

Appendix II: Description of data items from Carbonates query

Column Name	Column Description and Calculations	Format
Leg	Number identifying the cruise. The ODP started numbering the scientific cruises of the <i>JR</i> at Leg 101. A leg was nominally two months duration. During the 18+ years of the ODP, there were 110 cruises on the <i>JR</i> .	Integer 3
Site	Number identifying the site. A site is the location where one or more holes were drilled while the ship was positioned over a single acoustic beacon. The <i>JR</i> visited 656 unique sites during the course of the ODP. Some sites were visited multiple times, including some sites originally visited during the Deep Sea Drilling Program for a total of 673 site visits.	Integer 4
Hole	Letter identifying the hole. Multiple holes could be drilled at a single site by pulling the drill pipe above the seafloor, moving the ship some distance away and drilling another hole. The first hole was designated 'A' and additional holes proceeded alphabetically at a given site. Location information for the cruise was determined by hole latitude and longitude. During ODP, there were 1818 holes drilled or deepened.	Text 1
Core	Cores are numbered serially from the top of the hole downward. Cored intervals are up to 9.7 m long, the maximum length of the core barrel. Recovered material was placed at the top of the cored interval, even when recovery was less than 100%. More than 220 km of core were recovered by the ODP.	Integer 3
Coretype	All cores are tagged by a letter code that identifies the coring method used.	Text 1
Section	Cores are cut into 1.5 m sections in order to make them easier to handle. Sections are numbered serially, with Section 1 at the top of the core. Carbon/carbonate analyses were made on samples taken from the sections. Core Catcher sections identified as "CC."	Integer 2 or Text 2
Top Interval	The top interval of a measurement in centimeters measured from the top of a section.	Decimal F4.1
Bottom Interval	The location of the bottom of a sample in centimeters measured from the top of a section.	Decimal F4.1
Depth (mbsf)	Distance in meters from the seafloor to the sample location.	Decimal F7.3
Inorganic Carbon Percent	The weight percent of inorganic carbon in a sample.	Decimal F15.5
CaCO ₃ Percent	The weight percent of calcium carbonate in a sample. All inorganic carbon is reported as calcium carbonate. Inorganic_Carbon_Percent x 8.33 = CaCO ₃ _Percent.	Decimal F15.5
Total Carbon Percent	The weight percent of total carbon.	Decimal F15.5
Organic Carbon Percent	The weight percent of organic carbon in a sample. This value can be measured directly or calculated by subtracting the Inorganic_Carbon_Percent from the Total_Carbon_Percent.	Decimal F15.5
Nitrogen Percent	The weight percent of nitrogen in a sample.	Decimal F15.5
Sulfur Percent	The weight percent of sulfur in a sample.	Decimal F15.5
Hydrogen	The amount of hydrogen in a sample, in mg HC/g.	Decimal F15.5